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Mustard Press Cake Pyrolysis and Product Yield Characterization

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Abstract— Developing countries like India are facing a problem of higher waste generation due to increasing population. The shortage of disposal ground and stringent environmental rules are some of the main constraints of waste management. On the other hand the life of the conventional fossil fuel has become limited in the present era, where the use of energy and their source has been growing faster than the world population. The rigorous use of fossil fuel increases the emission rate of the green house gases which is a threat to the world climate. As a consequence, the world energy resources are exhausting and environment pollution is increasing. The world wide researchers are working to develop economical, energy-efficient processes and resources for production of fuels. In recent years pyrolysis method has been receiving great attention as a promising technology for producing char, bio-oil and gas. In this present investigation, mustard press cakes have been chosen as a source of renewable energy and as a pyrolysis feedstock. Experiments have been performed to determine the reaction kinetics. Temperature effects of pyro products yield have been discussed. CHNS and SEM analysis of char obtained from mustard press cake have been done. Pyro-oil yield was analysed using FT-IR.

Index Terms— Mustard press cake, pyrolysis, product yield, pyro-oil, SEM, FT-IR, CHNS.

1 Introduction

ENERGY is one of the most essential parts of developments of growing economy in a country like India. According to International Resource Group (IRG) [1], in the year 2003, India occupied fifth place as highest consumer in the world, in terms of primary energy consumption for accounting 3.5% of the world commercial energy demand. In current scenario, compared to other developed countries, India's position is little bit low due to rapid population growth, scarcity of conventional fossil fuels and diminishing reserves of crude oils. On the other hand, the utilization of conventional fossil fuels as energy resources generates green house gasses, mainly CO_2. The negative impacts of usage of conventional fuels on environment have forced the scientific community to recognize the importance of renewable and sustainable energy in recent years. Among several thermochemical conversion processes namely e.g., pyrolysis, gasification and combustion, in recent years pyrolysis have been receiving great attention as a promising technology for producing char, bio-oil and gas. The char might be used as solid smokeless fuels for barbeque, for the production of activated carbon or an adsorbent or for landfilling. The liquid products obtained from pyrolysis of biomass waste have been found highly oxygenated, viscous, corrosive, thermally and chemically unstable and chemically very complex [2]. It might be upgraded through removal of residues and by lowering the oxygen content. The gasious product might be used for all energy requirements of the pyrolysis plant due to its higher calorific value [3], [4], [5]. The yield of either of the products, namely, char or tar or gas might be maximized just by the adjustment of operating conditions. Among the lignocellulosic wastes generated in Indian cities, oil cakes of different oil seeds are one of the major constituents. Oil cakes are the solid effluent obtained from edible oil refineries. Due to high fat content oil cakes are not easily degraded and on the other hand pumgent odour is generated from the fermented mass of oil cake probably due to the presence of protein in it. Oil cake is a one kind of biomass, obtained after oil extraction from the seeds. Few studies have reported about the pyrolysis of oil cakes. Pyrolysis of various kind of oil cakes namely, seasame, mustard and neem de-oiled cake [6], jetropha oil cake [7], olive residue [8], rapseed cake [9], [10], pungam oil cake [11], sunflower oil cake [12] have already been done. Giannakopoulos et al. [13] has developed methods of pyrolysis by adding catalyst to the raw materials.

In this present investigation, mustard oil press cake has been chosen as a source of renewable energy and as a pyrolysis feedstock, since from an extensive literature survey it has been found that no detailed study is yet been done on mustard press cake through pyrolysis process. The mustard seed contains 42-49 % oil where the maximum is bulk press cake. India is one of the largest consumer and producer of mustard seeds. India has produced 6.32 million tons of mustard seeds in the year of 2009-2010 [6]. The detailed study on oil seed processing technology have reported that from 1 kg of mustard seed 320-350 g of oil can be derived and the leftover residue can be treated as biomass. The bulk mustard press cake is applied as cattle feed and fertilizers but major part is disposed unutilized. The oil cake is very rich in organic content and hence the dumping site of oilcake very often faces the problem of generation of waste water having high BOD value. According to Lo and Hill [14] the usage of mustard press cake as cattle feed has been decreasing since brassica juncea seeds meal (mustard press cake) contains high levels of glucosinolates (allyl isocyanates) which makes them unacceptable for animal

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consumption. Lo and Hill [14] and Srivastava et al. [15] have reported about the growth depression and toxic effects of glucosinolates in fishes due to disposal of oil cake.

2 Materials and Methods

2.1 Material

We have collected mustard press cake sample from a local oil mill near to Jadavpur University, Kolkata. The proximate and ultimate analyses of mustard press cake have been given in table 1. The ultimate analyses have been done using CHNSO analyser (2400 series-II, Perkin Elmer, U. S. A.). Calorific value of raw materials has also been determined using bomb calorimeter, given in table 1.

TABLE 1
PROXIMATE AND ULTIMATE ANALYSIS OF FEEDSTOCK

Property	Wt %
Moisture content	14.34
Volatile matter	63.49
Ash content	7.7
Fixed carbon	14.47
Carbon	40.26
Hydrogen	6.03
Nitrogen	6.46
sulphur	1.11
Oxygen	46.14
Gross calorific value (MJ/Kg)	14.56

2.2 Experimental

The pyrolysis experiment of mustard press cake was carried out in a 50 mm diameter and 640 mm long cylindrical stainless steel fixed bed pyrolyser (figure 1). The experimental procedure has already been discussed in previous study done by Chowdhury and Sarkar [16]. The morphological characteristics of mustard press cake and char produced from it at different temperature have been conducted through SEM (JEOL – JSM 5200) analyses. The ultimate analyses of both char and pyro-oil obtained at different pyrolysis temperature have been determined using CHNSO analyser. Calorific values of both products at different temperature have also been determined. FT-IR (VERTEX 70 FTIR) analyses of pyro-oil of different temperatures have been compared.

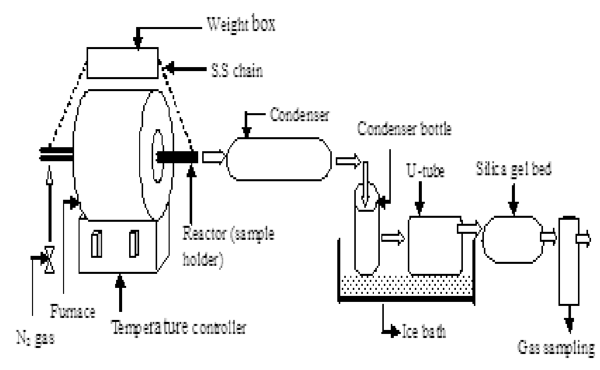

Fig. 1. Experimental set-up [16].

3 Pyrolysis Kinetics

Pyrolysis of mustard press cake proceeds through complex reactions in series, parallel or combination of both. In this present study a parallel reaction model has been attempted to describe pyrolysis kinetics. The reaction kinetics of volatile and char has been elaborately discussed in pyrolysis of coconut shell [17], vegetable market waste [18] and textile wastes [16]. The determination of frequency factors and activation energies of the reactions of reactant decomposition, volatile formation and char formation of this study [16], [17], [18] have also been followed. The frequency factors and activation energies of different reactions of pyrolysis of mustard press cake have been given in table 2. Where k, kv and kc is the rate constant for rate constant (min^{-1}), rate constant for volatiles formation (min^{-1}) and rate constant for char formation.

TABLE 2
CALCULATED ACTIVATION ENERGIES AND FREQUENCY FACTORS AS PER ARRHENIUS LAW

Reaction rate constant	Activation energy (KJ/mol)	Frequency factor (min^{-1})	Correlation coefficient
k	16.15	0.263	1.0
k_v	16.47	0.175	1.0
k_c	15.47	0.087	1.0

4 Result and Discussion

4.1 Effect of Temperature on Pyrolysis Product Yield

After completion of pyrolysis of mustard oil cake the solid residue was collected from the reactor. The amount of unreacted sample and the left char yield were determined. While the condensable part of volatile was considered as a tar yield, the organic part of tar, soluble in benzene was considered as pyro-oil. The gas yield was calculated by subtracting the amount of tar from volatiles yield.

Figure 2 has presented the distribution of product yields obtained from pyrolysis of mustard de-oiled cake in relation to the temperatures. It can be seen that char yield decreased with the rise in pyrolysis temperature. The char yield decreased from 37.7 wt% at 673K to 35.39 wt% at 1173K. The decrease of char yield with increasing pyrolysis temperature may be attributed to an increasing devolatilization of the solid hydrocarbons in the char. According to Ertas et al. [19] due to secondary decomposition of the solid product or huge amount of primary decomposition of the raw material at higher temperature, the char yield decreased with increased pyrolysis temperature. Partial gasification of the carbonaceous residue was another reason of this behavior [20]. In case of tar yield, it was found that the tar yield increased from 23 wt% to 46 wt% when the pyrolysis temperature was increased from 673K to 973K and then suddenly it decreased to 35 wt% at 1173K. Similar trends of tar yield have been observed by many others researchers namely, Ertas et al. [19], Raja et al. [11], [7] and Pstrowska et al., [21] in case of pyrolysis of laurel (Laurus nobilis L.), jetropha oil cake, pugam oil cake and rapeseed oil cake respectively. From different literature studies it has been concluded that the reason behind the decreasing of tar yield at higher pyrolysis temperatures is due to the decrease of the organic and specific product and secondary volatiles decomposition above 773K [22], [23]. On the other hand the gas yield increased gradually with increasing temperature. The increase in gaseous products may be due to the secondary cracking of the pyrolysis vapours at higher temperature.

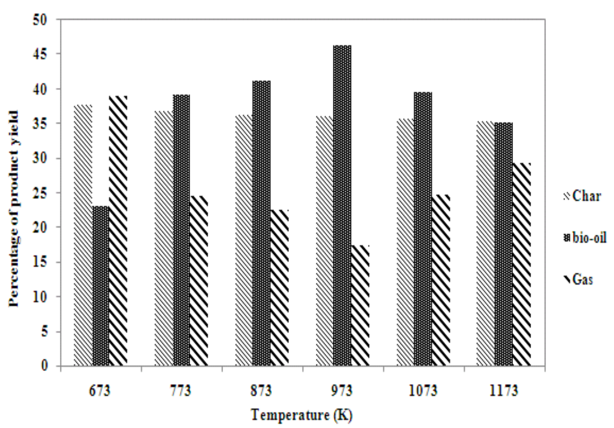

Fig. 2. Percentage of product yields as char, tar and gas of mustard oil cake in different pyrolysis temperature (K)

4.1 Characterization of Product Yield of Mustard Press Cake

Ultimate analysis of char and pyro-oil

The ultimate analyses of char and pyro-oil have been conducted using CHNOS analyser. Effect of pyrolysis temperature (773K, 973K and 1173K) on elemental composition of char and pyro-oil has been shown in table 3. It has been observed that fraction of carbon increases with pyrolysis temperature up to 873K and beyond 973K it decreases. This may be due to the fact that in the initial span of temperature from 673K to 873K, carbon enrichment of char occurs due to evolution of lower molecular weight volatiles. However above 973K, cracking of char as well as heterogeneous secondary reactions involving char and gaseous products cause depletion of carbon fraction in char. On the other hand, fraction of hydrogen in char monotonically decreases as they have the tendency to appear in the more volatile lower molecular weight volatile products.

TABLE 3
ULTIMATE ANALYSIS OF MUSTARD OIL CAKE CHAR AND PYRO-OIL AT DIFFERENT TEMPETATURES

Sample	T (K)	C %	H %	N %	S %	O %
Char	773	38.12	1.09	4.10	0.52	56.17
	973	36.88	1.68	4.46	0.65	56.33
	1173	35.62	0.00	0.73	0.27	63.38
Pyro-oil	773	52.37	8.55	8.91	1.15	29.02
	973	58.53	6.36	6.08	0.56	28.47
	1173	54.00	6.00	5.78	1.42	32.8

FT-IR analysis of liquid fuel

The pyrol-oil obtained from mustard press cake was characterized for the presence of functional group and figure 4 has shown the FT-IR (VERTEX 70 FT-IR) spectra for pyro-oil obtained from mustard press cake at different temperature. Band assignments of IR spectrum of pyro-oil, which were summarized in table 4, indicate that the pyro-oil contains a number of atomic groupings and structures.

TABLE 4
THE MAIN ATOMIC GROUPS AND STRUCTURE OF PYRO-OIL OF MUSTARD OIL CAKE

Wave number (cm^{-1})	Infrared spectrum	Atomic groups and structures
3200-3700	O-H stretching	Hydroxyl
2800-3000	C-H stretching	Aliphatic structures
1650-1770	C=O stretching	Carbonyl
1610-1680	C=C stretching	Oliefinic structures
1450-1600	C=C stretching	Aromatic structures
1420-1480	C-H bending	Aliphatic structures

The bands due to the atmospheric contributions of water vapor and CO_2 have been subtracted from the spectra in order to improve the spectral quality. The intensity of spectrum of pyro-oil has changed with the increase of temperature. The intensity of the transmission due to the hydrogen bonded OH stretching decreased with increase in pyrolysis temperature. The decrease may be due to the loss of phenolic or alcoholic groups since the oxygen/carbon (O/C) ratio of the pyro-oil also decreased at high temperatures [24]. The band due to the OH stretching vibration was still present at 973K. This band must be due to phenolic hydroxyls since all the aliphatic groups have disappeared at this temperature. The broad band for the OH in-plane bend also decreased with increase in temperature. A band above 3400 cm^{-1} corresponding to free OH stretching vibrations, changed with increased pyrolysis temperature. The reason behind this was increased carbonization of the sample. The CH_3 stretch of the O–CH_3 group appeared at 2842–2839 cm^{-1} in pyro-oil and its intensity decreased as the temperature increased from 673 to 973K. The band was decreased above 773K, indicating that the CH_3 groups were removed from the substituted aromatic rings at high temperatures. A similar behavior has been observed by the OC stretch (at1033 cm^{-1}) in the methoxyl group. With the increase in temperature the intensity of the stretch decreases. The band due to the aliphatic CH stretch had a high intensity at 673K but the intensity decreased with increase in temperature and the band became weak at 973K. The most suitable band for monitoring the aromatic nature of the pyro-oil was probably the band due to the aromatic CH stretch. The intensity of the band at 3064 cm^{-1} increased with temperature, especially above 673K. This shows that the extent of aromatic substitution decreased at high temperatures, consistent with the decrease in the oxygen containing groups at high temperatures. Since the number of adjacent aromatic hydrogen atoms may provide an estimate of the degree of aromatic substitution and condensation, the variations in the aromatic CH in the 900–700 cm^{-1} region were used to study the changes in the aromatic structures. The band due to the aromatic ring mode decreased at high temperatures and disappeared above 673K. The band for the lone aryl CH wag shifted upward to 859 cm^{-1} at 673K, and to 881cm^{-1} at 973K, suggesting a change in the chemical nature of the band. The locations of this band in naphthalene, substituted naphthalene, and anthracene are 875–823, 905–835 and 900–875 cm^{-1}, respectively [25]. However, due to differences in the intensities of the FTIR signals and the amounts of sample in different analysis, the concentrations and path lengths were also different in various analyses. As a result, only the ratios of the peak areas with respect to a reference peak were compared. The band at 1597 cm^{-1} represented the aromatic ring mode.

SEM analysis and characterization of feedstocks and char

Micrographs of SEM (Scanning Electron Microscope) (JEOL – JSM 5200) analyses with magnification of 15KV X 100 of mustard oil cake and char after pyrolysis of feedstock at 773K for 1 hour are shown in figure 3. Micrographs are examined to characterize the shape and the size of the char particles, as well as their porous surface structure. From a phenomenological point of view, a gradual release of different volatile compounds occurs as the temperature increases during devolatilization in high temperature range. It appears that at a higher temperature, the devolatilization is more intense making the char more porous.

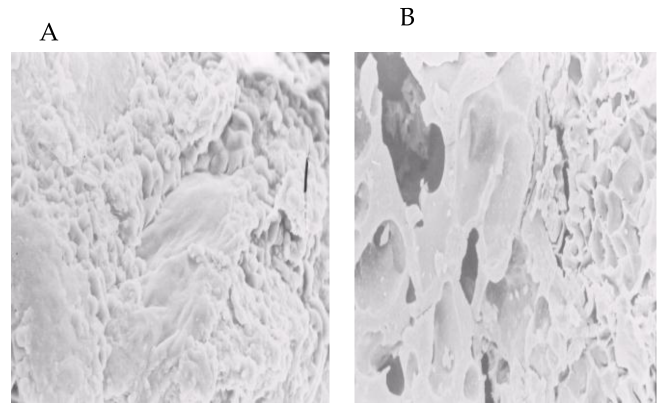

Fig. 3. SEM photomicrographs of (A) original mustard oil cake sample (B) chars obtained at pyrolysis temperatures of 773K

Physical properties of char and pyro-oil

Table 5 has been presented the comparison of fuel properties of commercial fuels with pyro-oil obtained from mustard press cake. Fuel properties namely, density, pH, boiling range, calorific value is known to be typical key properties for combustion in boiler, furnace and engines. It can be inferred that the pyro-oil obtained from mustard press cake is highly viscous compared to diesel. High viscosity leads to poor atomization and incomplete combustion of the fuel, formations of excessive carbon deposits on the injection nozzles and which is desirable to avoid corrosion in the pipelines and storage tanks.

TABLE 5
PHYSICAL PROPERTIES OF PYRO-OIL COMPARED TO COMMERCIAL DIESEL

Characteristics	Mustard oil cake	Commercial diesel
Appearances	Dark brown	Yellowish
Specific gravity	1.084	0.84
Viscosity	Highly viscous	2.7 cst at 40°C
pH	8.7	5.6
Boiling range	100-185°C	250-350°C

Calorific vales of char and pyro-oil

The calorific values of pyro-oil and char of mustard press cake obtained at different pyrolysis temperatures has been determined using bomb calorimeter. The calorific values of char and tar of mustard oil cake at different temperature have been given in figure 4. The calorific values of pyro-oil of mustard oil cakes decrease gradually as temperature increases from 673K to 773K or 873K. Beyond 673K the calorific value decreases as the temperature is changed from 673K to 1173K. Pattern of temperature dependence of calorific value of pyro-oil is also similar to that of char. This may be justified by the fact that fraction of carbon in char decreases as the temperature increases up to 1173K, and at this time duration char participates in heterogeneous reactions with gaseous product. In case of tar, secondary cracking of tar takes place causing decrease in calorific value of tar.

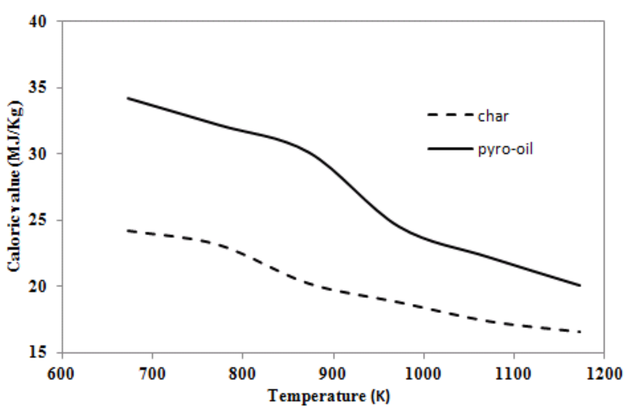

Fig. 4. Calorific values of char and pyro-oil at different temperature (K)

5 CONCLUSION

In this present study, the mustard press cake which is an agricultural waste was chosen as a pyrolysis feedstock to produce pyro-oil and char. The effect of temperatures (673K to1173K) on product yields has been studied. These parameters have shown significant effect on pyrolysis product yields. SEM analysis of mustard press cake and the char produced from it at temperature of 773K have been done. Micrographs characterize the shape and the size of the char particle, as well as their porous surface structure. FT-IR analyses of pyro-oil obtained from mustard oil cake at different temperatures has been performed. The effects of pyrolysis temperature on calorific values of tar and char obtained from mustard oil cake at different temperatures from 673K to 1173K have been discussed.

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